

BIOMASS AND COAL FLY ASH AS CEMENT REPLACEMENT ON MORTAR PROPERTIES

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Abstract. Nowadays, construction sector tries to implement several options to minimize issues related to concrete sustainability. The main goal of this work was to study the effect of biomass fly ash, blended with coal fly ashes or alone, as cement replacement in mortars properties. Three replacement percentages were tested (20, 40 and 60 %wt). Fresh and hardened properties (mechanical strength along time of curing) were evaluated. Mortars with biomass fly ashes have shown lower workability than the reference one. Mortars with 20% of cement substitution presents better results for all curing times. However, in the three percentages of substitution, and for all curing periods, the best results were found for mortars composed with biomass fly ashes. This work showed that is possible to use biomass fly ashes as partial cement substituent with good results in terms of durability and quality of concrete. Its utilization at an industrial level of concrete production can decrease the energy and raw materials consumption related to cement production and allows a more sustainable option on the ash management.

1 INTRODUCTION

Concrete is the most used material on building mainly by the fact of present good mechanical and durability properties [1]. However, concrete has a significant impact on environment, since high content of natural resources and energy flows are necessary to its production. Furthermore, it is known that to produce one of the most important materials used on concrete (Portland cement) a significant emission of CO₂ is released to atmosphere, and this is related with the greenhouse gases effect and with the global warming of planet [2].

Nowadays, the environmental questions are very important in all economical sectors. The

construction sector deals with the issue of find several options that can be implemented to minimize problems related to concrete sustainability [3]. One of them, is the use of supplementary cementitious materials (usually called as pozzolan), which offer a potential reduction in global CO₂ emissions [4], reduce the cost of concrete production, may enhance the workability of fresh concrete and in some cases improve the durability of concrete [1].

Coal fly ash (FA) is the most artificial pozzolan used in concrete production [1]. FA has several advantages when compared with cement, such as lower hydration heat, is a by-product of coal combustion and is cheaper than cement [2].

Countries like Portugal, which are interested in increase the energy production using renewable sources, like biomass, are now interested and deal with different issues. The use of biomass to produce energy by combustion increased in the last years, on the other way, several economical sectors use biomass as raw material to produce heat and power [4]. The increase on its use led to a significant issue related with the increase of biomass fly ash (BFA) that needs to be solved. Fly ash from biomass combustion is classified as solid waste and usually is managed by disposal in landfill. However, disposal in landfill has economic, environmental and sustainable issues [4]. In other countries, in some cases they are recycled on agricultural fields or forest, but in most cases without any form of control [5]. BFA can be used as a pozzolanic material, such as fine aggregate or as binder in cement-based materials and some studies showed good results when BFA was incorporated in concrete [6]. On the contrary to coal fly ash, biomass fly ash still need more significant researches about its usage and its commercial utilization is not yet widely reported [7].

Thereby, the main goal of this work was the production of mortars using BFA and blends of biomass and coal fly ash as substitute of cement and studied its effects on mortars properties. On fresh state workability was evaluated and on hardened state its mechanical and durability properties were determined.

2 MATERIALS AND METHODS

2.1 Coal and Biomass Fly ash

BFA was sampled in a Portuguese pulp and paper industry, which used forest residues, such as bark from eucalyptus and pine, as fuel to produce heat and power. FA was sampled from a Portuguese thermoelectric power plant. Both ashes were characterized in terms of particle size distribution, loss on ignition, chemical composition and thermal analysis.

The particle size distribution of ashes was determined, in a liquid environment, by laser diffraction using CILAS 920 equipment. The ashes were grinded in order to obtain samples with particle size lower than 90 µm for its characterization in terms of loss on ignition (LOI), chemical and thermogravimetric analysis. For the LOI and chemical composition the milled samples were previous dried at 101±1°C. LOI was determinate in an approximately 1.5 g of dried sample heated at 1100°C during 3 hours in a Carbolite furnace. The chemical composition was determined by X-Ray Fluorescence using a Panalytical Axios spectrometer. The thermal analysis was done using a STA, Netzsch 402 EP with a heating rate of 10°C/min.

2.2 Mortar Formulations

A group of sixteen formulations of mortar (Table 1) was set with the utilization of BFA as

substituent of cement and the utilization of the same ash but blended with FA. In those formulations a CEM I 42.5R (Outão, Secil) cement was used and a commercial river rolled sand 0/4 mm was used as aggregate. Three levels of cement substitution were studied: 20, 40 and 60 %wt. All mortar mixtures were made with 1 wt. part of binder (considered as the sum of cement plus fly ash): 2.5 wt. parts of aggregate and water-binder ratio (W/B) of 0.5. For each mixture three mortars were performed.

Table 1: Mortar Formulations

| Mortar Codes | % of cement substitution | % of FA - BFA |
|--------------|--------------------------|---------------|
| FA0 | 0 | 0 |
| FA20 | 20 | 20-0 |
| FA16-BFA4 | 20 | 16-4 |
| FA12-BFA8 | 20 | 12-8 |
| FA8-BFA12 | 20 | 8-12 |
| BFA20 | 20 | 0-20 |
| FA40 | 40 | 40-0 |
| FA32-BFA8 | 40 | 32-8 |
| FA24-BFA16 | 40 | 24-16 |
| FA16-BFA24 | 40 | 16-24 |
| BFA40 | 40 | 0-40 |
| FA60 | 60 | 60-0 |
| FA48-BFA12 | 60 | 48-12 |
| FA36-BFA24 | 60 | 36-24 |
| FA24-BFA36 | 60 | 24-36 |
| BFA60 | 60 | 0-60 |

2.3 Fresh and hardened properties of mortars

The workability was expressed as reach spread diameter in mm and determined after 15 strokes of the flow table according to EN 1015-3:1998 [8].

The mortar specimens for the mechanical resistances and water absorption tests were prepared in a standard mixer, were placed in 40x40x160 mm³ moulds and compacted two times. The moulds were covered with plastic film to avoid the loss of water and stored in a humidity chamber (with approximately 87 % of relative humidity and 21 °C of temperature) during 24h. After that time, the mortars were demoulded and again stored in the humidity chamber, according to [9]. The flexural strength was determined in a LLOYDS Instruments universal testing machine (with a maximum capacity of 50 kN), the compressive strength was measured in an Ele Auto Test press (with a capacity between 5 to 110 kN). The mechanical strength tests were done according to EN 1015-11:1999 [9], on three samples for each formulation, for mortars with 2, 7, 28, 90 and 180 days of curing. After 28 days of curing, mortars for water absorption analysis were tested for flexural resistance and then one part of each mortar were used to capillarity test and the other was used for the immersion test. All the mortars parts were dried at 60±5°C until mass reached constant before water absorption tests, which were

done according to [10–13]. The coefficient of water absorption by capillarity is defined by the representation of a straight line linking the points of the measures carried out between 10 and 90 minutes and calculated based in Eq.1 [12].

$$C = 0.1(M1-M0) \quad (1)$$

Where,

C is the coefficient of water absorption $\text{kg}/(\text{m}^2 \cdot \text{min}^{0.5})$

M1 is the mass (g) of the specimen after soaking for 90 min;

M0 is the mass (g) of the specimen after soaking for 10 min.

The immersion water absorption is determined as present in Eq.2 [13]:

$$A_i = \frac{M_1 - M_3}{M - M_2} \times 100 \quad (2)$$

Where,

Ai is the water absorption by immersion;

M1 is the mortar mass on air saturated (g);

M2 is the hydrostatic mass of the saturated mortar (g);

M3 is the dry mass of mortar (g).

The shrinkage test was done to the mortar formulations that presented the best results, in terms of mechanical resistances after 28 days of curing and for each level of cement replacement. To measure the shrinkage and weight loss three prisms with $25 \times 25 \times 250 \text{ mm}^3$ for each mixture were moulded. The moulds to this experiment have a system that allows the application of stainless steel bolts in the specimen tips. The shrinkage was determined on specimens after demoulded. After that time the mortars were putted in a climatic chamber with a temperature and relative humidity control (temperature 20°C and moisture content of 60%), where the shrinkage measuring equipment was also stored.

3 RESULTS AND DISCUSSION

3.1 Characterization of material used on mortar formulation

The particle size of the fly ashes is presented in Figure 1. Since the ashes were used as cement substituent, the particle size distribution of cement (CEMI 42.5) was also analyzed.

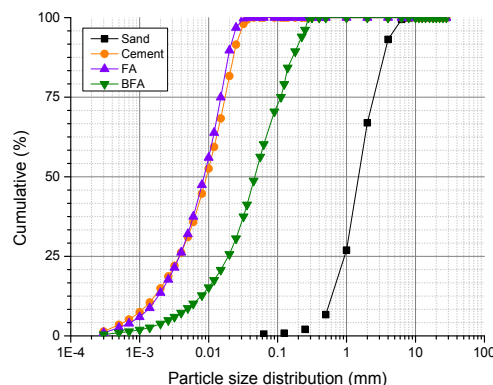


Figure 1: Cumulative particle size distribution.

The particle size distribution of FA is similar than for the cement with an average diameter of about 9 μm . However BFA presented coarser particles and its size distribution is significantly different than coal fly ash and cement. The average diameter of BFA is about 47 μm .

The obtained LOI and the chemical composition of the materials used in mortars are showed in Figure 2. As it can be seen, BFA showed the highest value for LOI (>5% dry bs), followed by FA, cement and sand. As expected, Si was the major chemical element present in sand and calcium in cement. Si was also the major chemical element (>25 %, dry bs) present in the FA, followed by Al, Fe, Ca and K. In contrast, Ca was the major chemical present in BFA (>19 % dry bs), followed by Si, Al, K, Fe, Mg. An interesting observation was the fact that only the BFA showed in its composition Cl and S and this is also due to the inorganic content of biomass [15], but also is due to the fact of these ashes have the capacity of allows the adsorption of those chemical elements, in the form HCl and SO₂, from the gases during biomass combustion [16].

In terms of minor chemical elements, the two fly ashes were enriched when compared with cement and sand. Among the minor chemical elements Ba presented the high value followed by Zn, Sr, Zr, Rb and Cu for the BFA sample. In the case of FA, Sr was the minor chemical element with higher concentration followed by Ba, Br, Zr, and Cr.

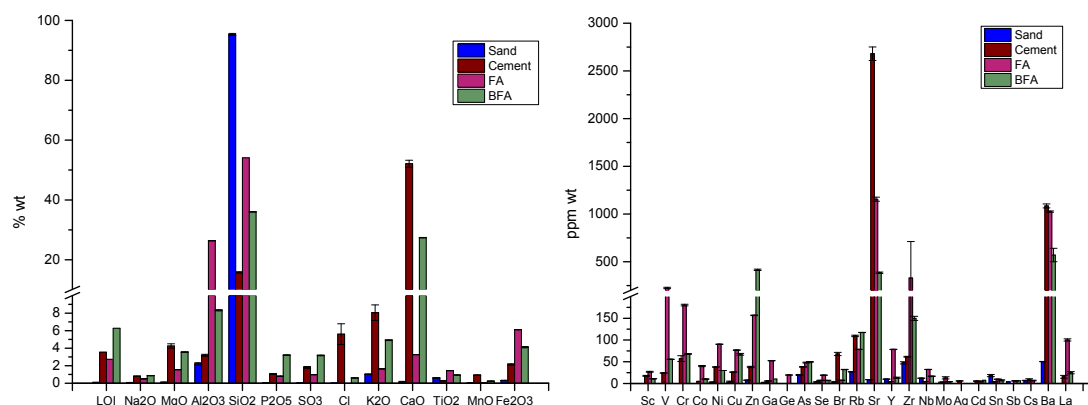


Figure 2: Loss on ignition and chemical elements concentration in the materials used in mortar formulations.

The TG and DTA signals registered for cement, FA and BFA are shown in **Error! Reference source not found.** It was observed a slight decreased around of 100°C for both ashes, this loss of weight is related with the release of water adsorbed in the ash. In the BFA, a slight increase on the weight near 430°C was observed and this is related with the change of the iron phase. With increasing temperature, a significantly decrease in weight of the two fly ashes is observed in the range of 600 to 835°C, associated with an endothermic process. This weight loss must be related to the thermal decomposition of carbonates like CaCO₃. The total weight loss was approximately 2-3 % for the FA and 6-7 % for BFA and these results are similar to the value observed for LOI analysis (Figure 2).

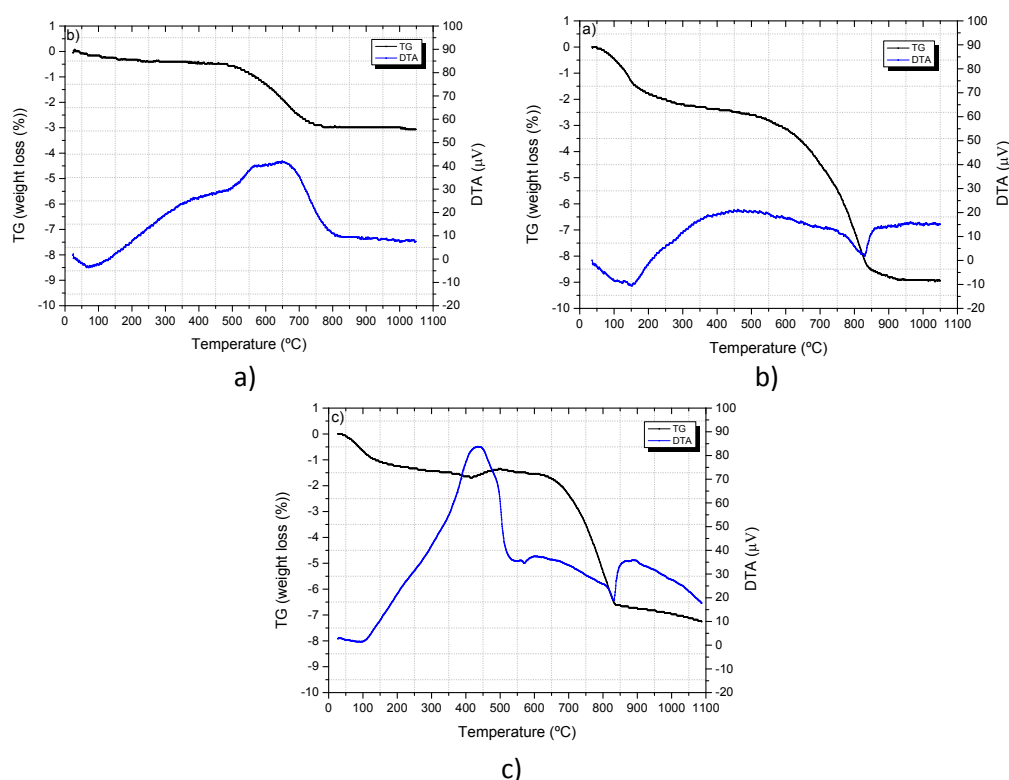


Figure 3: Thermogravimetric analysis of Cement (a), FA (b) and BFA (c)

3.2 Mortar fresh properties

The flow spread obtained results are presented in Figure 4. The values obtained for the studied formulations showed that mortars with fly ashes had low spread value than the reference mortar (FA0). However, the differences are, in general not relevant except for mortars made without FA and BFA replacement percentages higher than 40%. The incorporation of only FA did not present a significant influence in the flow spread when compared with cement. On the other side, it was observed a decrease on the flow spread value with the increased of cement substitution by BFA (alone or blended with FA) when compared with the reference mortar. The lower value was observed for the mortar with 60% of cement substitution by BFA. These results are explained by the physical characteristics, mainly the irregular shape settles on the high specific surface area. Furthermore, the presence of significant organic matter content could support the adsorption of the water molecules [6], leading to the flow spread value decrease.

3.3 Mortar hardened properties

The flexural strength values of mortars containing BFA or/and FA and of the reference mortar are shown in Figure 5.

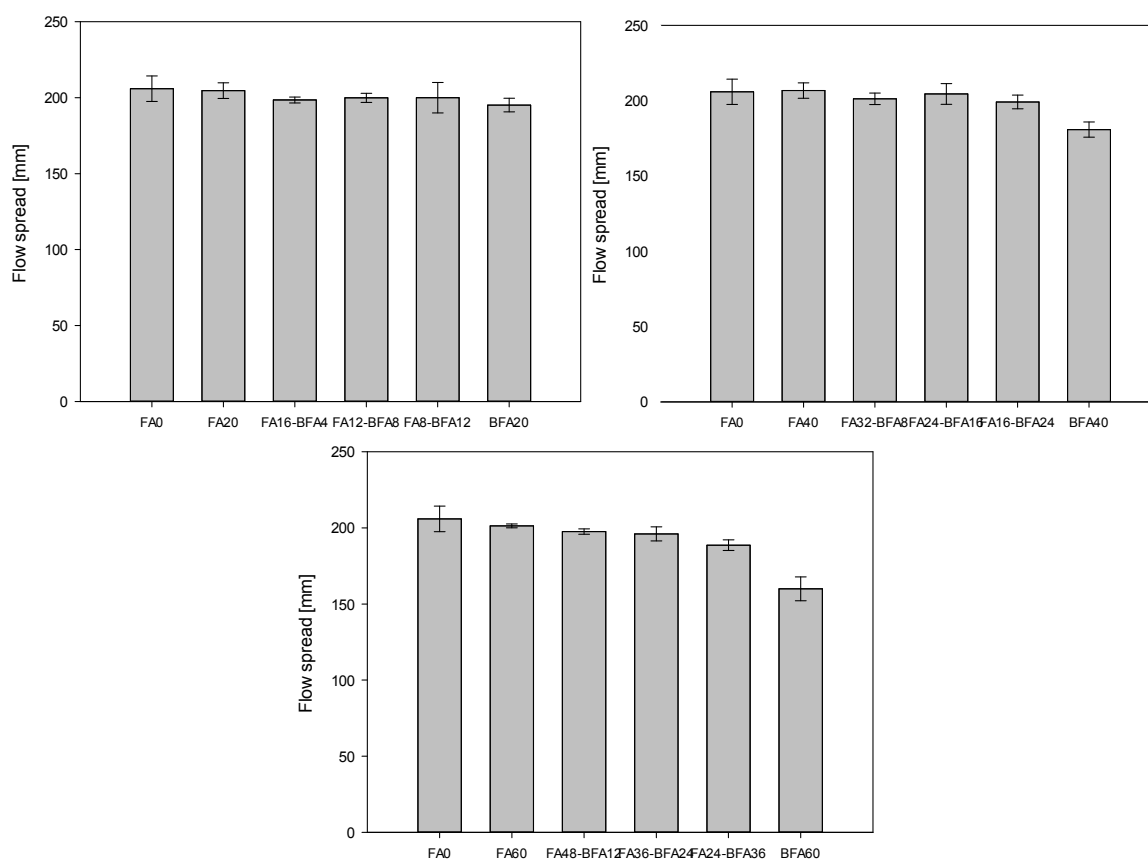


Figure 4: Values of flow spread of mortars prepared with different fly ashes incorporations

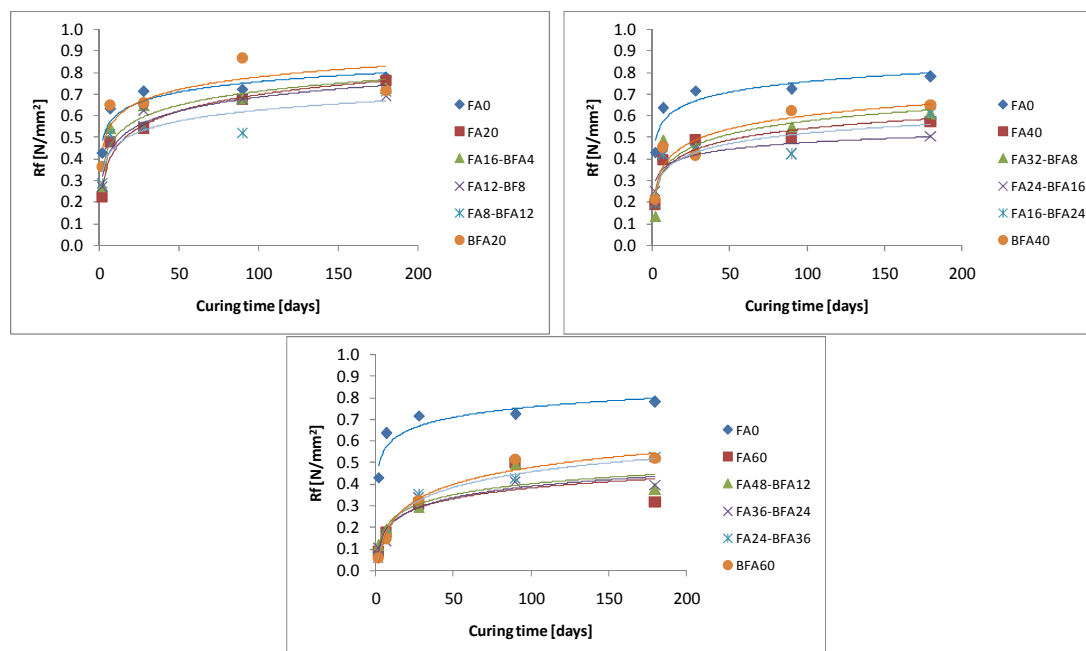


Figure 5: Evolution of flexural strength values of mortars up to 180 days of curing

As it can be seen the values of the flexural strength for all mortars made with BFA and/or FA at 2 curing days were lower than for the reference mortar and a significant decrease was observed for all mortars with 60% of cement substitution. In mortars with 20% of cement replacement and with 2 curing days, an increase was observed with the BFA increment, being the highest value observed for mortars with 20% of cement replaced by BFA. For the other curing periods, the flexural strength values of the mortars with 20% of cement substitution (FA20 to BFA20) were slightly lower than for the reference mortar, with the exception of BFA20 at 90 days that presented a higher value than the reference, being the better values observed on BFA20 (20% of BFA). For the other cement replacement percentages, the flexural strength values were lower than the reference, being the better values once again observed for mortars with cement replaced by BFA.

The values for compressive strength of mortars are shown in Figure 6. As it can be seen, the compressive strength values of all mortars with BFA or FA and for the different curing periods showed lower values than the reference mortar, with the exception of FA16-BFA4 for 180 curing days.

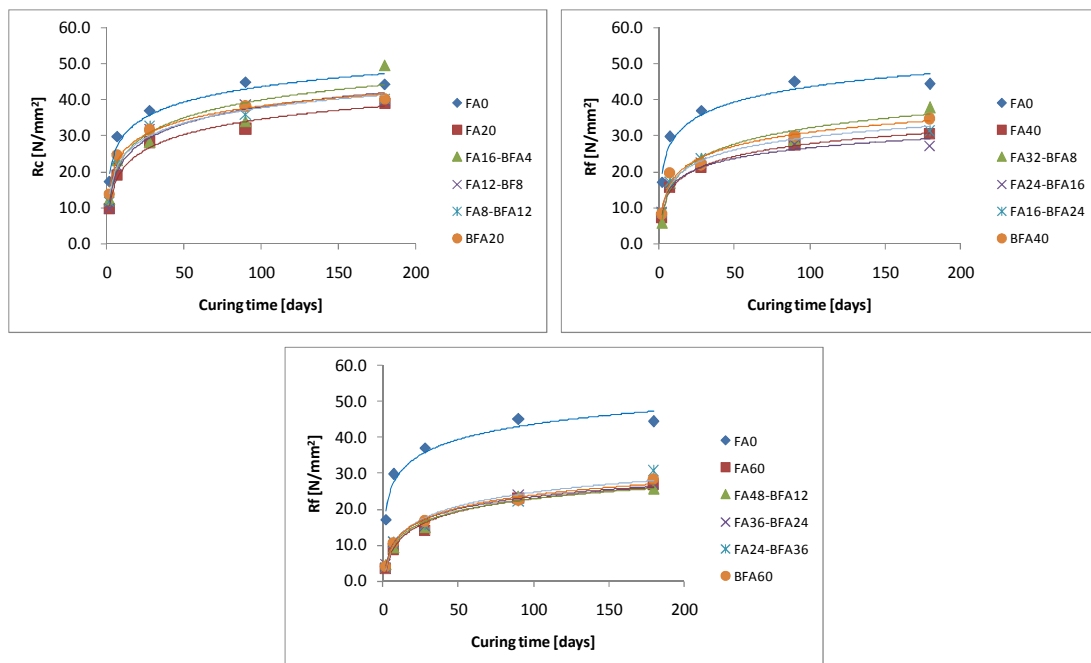


Figure 6: Evolution of compressive strength values of mortars up to 180 days of curing

The values increased with the curing time and this is related with the fact of pozzolanic materials show low early strength and a higher development on strength with age [17]. Mortars with 20% of cement substitution presented the better results when compared with the reference mortar for all curing time. It was observed, that an increase on the biomass fly ash content allows an increase on compressive strength.

For the other percentages of substitution, no significant differences were observed between mortars with FA, blended and BFA only. However, in the three percentages of substitution, and for all curing periods, the best results were found for mortars composed by BFA, followed by the mortars with more content of BFA on the blends. The lower values of

compressive strength for mixtures with coal and/or biomass fly ash compared to the ones made without cement replacement can be due to its particles, which are coarser than coal fly ash and may leads to an increase on the porosity of mortars [18].

3.1.1 Water absorption

The influence of the presence of fly ashes on the water absorption by capillarity of mortars (after 28 days curing) is shown in Figure 7. Mortar with 20% of cement replacement showed lower values of water absorption for mortars with high BFA content (FA8-BFA12 and BFA20) when compared with the reference concrete (FA0).

Concrete with 40% of cement replacement by FA (FA40) exhibited higher values than the reference. However 40% of BFA led to similar capillary water absorption than for plain cement mortar (BFA40). Formulations with 60% of cement presented high values for water absorption by capillarity when compared with the reference ones, with an exception of BFA60 formulation.

Figure 8 demonstrates the values of open porosity obtained from the water absorption by immersion test for all mortar formulations. As it can be seen, all mortars exhibited higher values for water absorption when compared with the reference mortar. The presence of BFA seems to have a slight positive effect when compared to the values obtained for FA mixes.

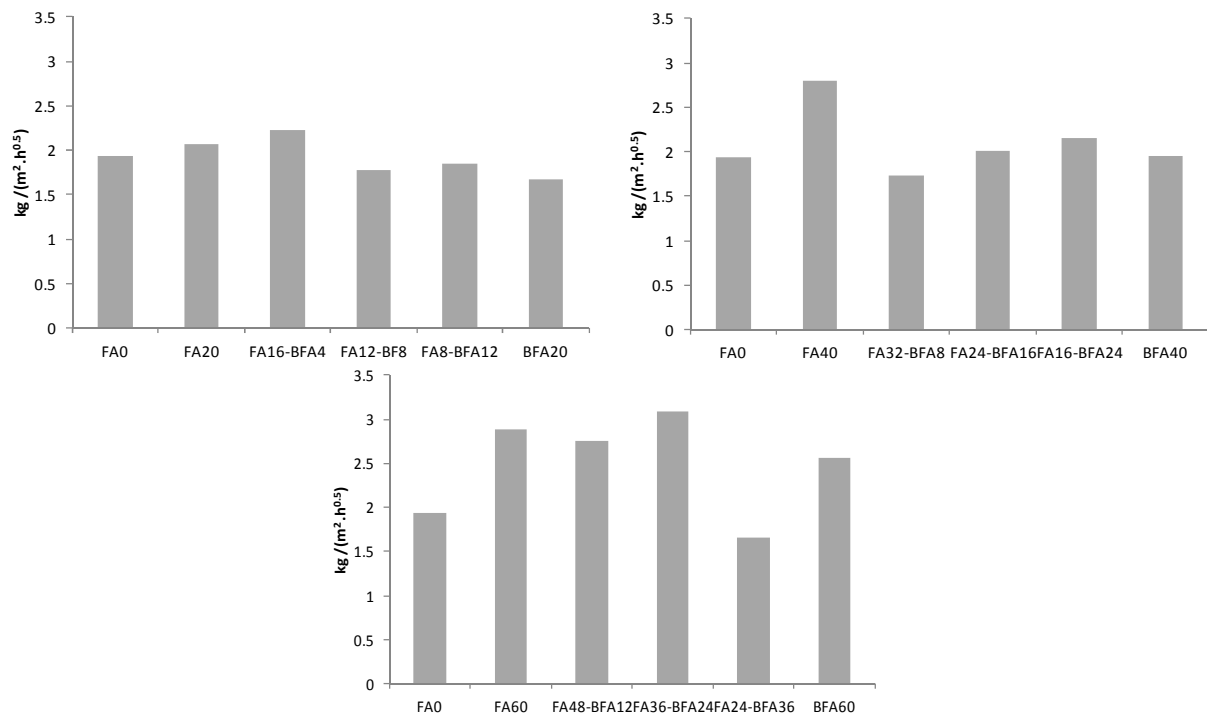


Figure 7: Water absorption capillarity coefficient for the different formulations

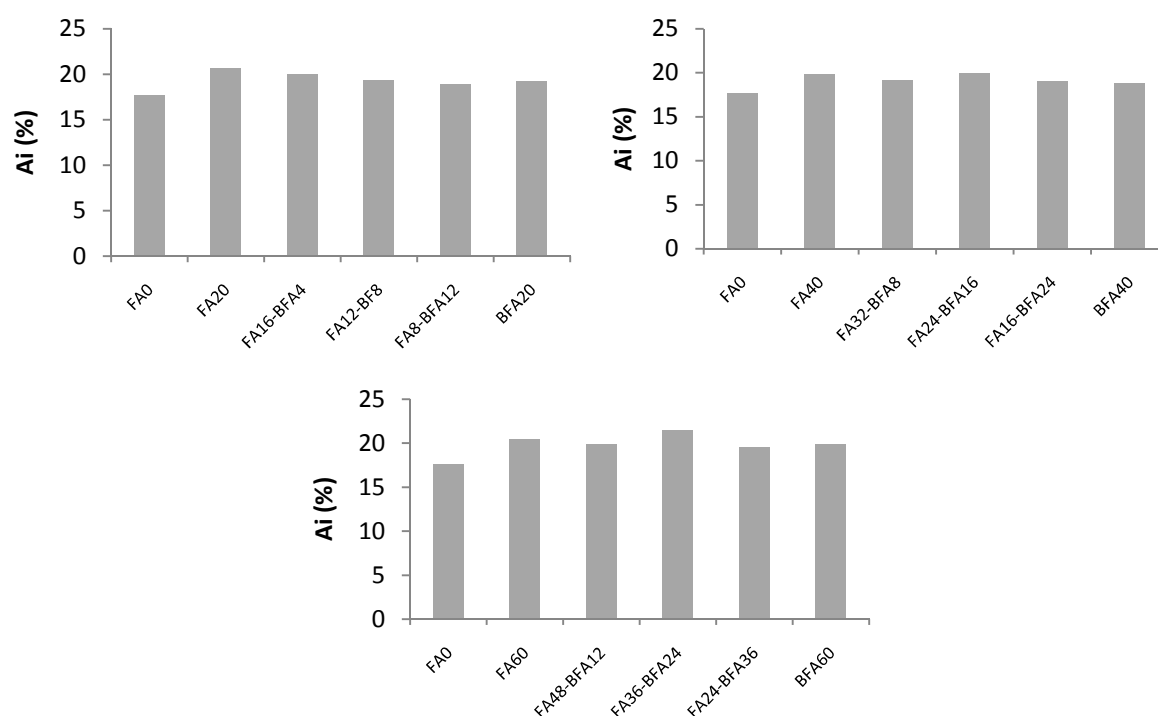


Figure 8: Values for water absorption by immersion (expressed in %) for the different mortar formulations.

3.1.2 Shrinkage

The shrinkage behavior of mortars along the time and with the different content of the selected fly ashes is presented in

Figure 9. It was observed a higher rate of shrinkage during the first 14 days. After that period, the shrinkage values were still growing but with a lower rate. The incorporation of fly ashes reduced the shrinkage of mortar at a later age and all values were lower than for the reference mortar. Similar results were verified in [19].

The weight loss was similar for the different mortars at early ages, however after approximately 5 days differences was observed. In this case, the mortar with higher content of fly ashes and with a higher percentage of cement substitution showed the highest weight loss values. These results showed that despite the formulations with high content of fly ashes present the higher weight loss values did not present the higher values for shrinkage. This could be related with the fact of shrinkage is affected by others parameters in addition to weight loss, like porosity, mortar only with cement present a finer pore structure and this could lead to the increase on the shrinkage values (Gesoglu et al., 2004). Other explanation for this could be related with the different types of shrinkage, the decrease on cement content on mortars with fly ash could decrease the effect of autogenous shrinkage and for that the drying shrinkage is more significant.

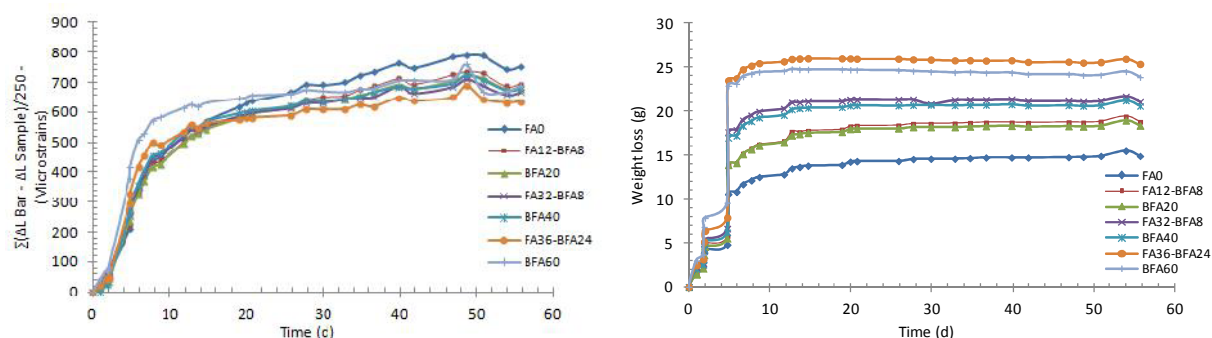


Figure 9: Average values for shrinkage and weight loss with time of the different mortars formulations

9 CONCLUSIONS

Mortars with BFA exhibited slightly lower workability than the reference. It was observed a decrease on the flow spread diameter with the increased of cement substitution by BFA. Mortars with 20% of cement substitution presented better results for all curing time, in terms of mechanical strength and water absorption. However, in the three percentages of substitution and for all curing periods the best results were found for mortars composed with BFA. The replacement of cement by FA and/or BFA benefited and mitigated the total shrinkage of the mortars.

In short, this work showed that it could be possible to use biomass fly ashes as partial cement replacement with good results in terms of durability and quality of concrete. Its utilization could be important to mitigate the issues related to high volume fly ash content and can be used for the production of concrete with characteristics similar than a high volume fly ash concrete but with a better environmental performance.

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